Fluorescent Conjugated Polymers That Incorporate Substituted 2,1,3-Benzooxadiazole and 2,1,3-Benzothiadiazole Units

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ABSTRACT: Heterocyclic monomers based on 2,1,3-benzooxadiazole and 2,1,3-benzothiadiazole bearing solubilizing side chains have been synthesized in high yields over three steps from readily available starting materials. The monomers are efficiently cross-coupled with diynes and bis(boronates) to afford high molecular weight luminescent poly(arylene ethynylene)s and polyfluorenes that exhibit red-shifted absorption and emission maxima, greater solubility, and reduced aggregation.

Introduction

The incorporation of conjugated heterocyclic units can greatly influence the properties of conjugated polymers. Among these, 2,1,3-benzothiadiazole has been incorporated in a growing number of low-band-gap materials, in large part due to the ease of preparation of 4,6-dibromo-2,1,3-benzothiadiazole.[1] This heterocycle has been incorporated in electroluminescent dyes[2] and polymers[3] to generate efficient green to red OLEDs. Conjugated materials that incorporate 2,1,3-benzothiadiazoles also include fluorescent dichroics that align in liquid crystal matrices,[4] electrochromic polymers,[5] and low-band-gap poly(arylene ethynylene)s.[6] Finally, energy transfer to a 2,1,3-benzothiadiazole-centered lower energy site has been utilized in the development of biosensors for single-strand DNA and alkaline phosphatase activity.[7]

In view of the broad utility and popularity of the 2,1,3-benzothiazole unit, it is surprising that the synthesis of analogues or derivatives of this heterocycle and their successful application to conjugated materials have only rarely been reported.[8] For instance, the incorporation of the oxygen analogue, 2,1,3-benzooxadiazole, into conjugated materials has until recently[9] only been claimed in patents[10] and in accounts of corporate research[3a,b] in which details of synthesis and characterization are scarce. That few conjugated materials incorporating 2,1,3-benzooxadiazole have been reported is surprising in view of the well-known intense fluorescence of some of its derivatives, such as NBD-Cl (4-chloro-7-nitrobenzo-2,1,3-oxadiazole), a widely employed fluorescent probe for amines.[11]

Herein, we report the synthesis of new electron-deficient monomers based on the 2,1,3-benzothiadiazole and 2,1,3-benzooxadiazole heterocyclic cores and their incorporation into conjugated polymers of the polyfluorene and the poly(arylene ethynylene) families. These new monomers bear side chains at the 5- and 6-positions, resulting in improved solubility and reduced propensity to irreversibly aggregate. The properties of conjugated polymers that incorporate these monomers are compared to those derived from an unsubstituted 2,1,3-benzooxadiazole heterocyclic core.

Results and Discussion

The 5,6-dialkoxy-4,7-dibromo-2,1,3-benzooxadiazole monomer **4** is prepared in good yields over three steps starting from the readily available 1,2-dialkoxy-4,5-dinitrobenzene (**1**) (Scheme 1). Treatment of **1** with sodium azide in dimethyl sulfoxide at 100 °C affords the benzofuroxan **2** in excellent yield, presumably through a *o*-nitroazide intermediate generated in situ.[12] Deoxygenation with triphenylphosphine in an aromatic solvent[13] was found to provide better yields of benzofurazan **3** than the use of triethyl phosphite. For increased simplicity, these two steps can be combined in a single-pot reaction by performing the reaction with sodium azide in toluene in the presence of a phase-transfer catalyst and then directly adding triphenylphosphine to the reaction mixture to result in the conversion of **1** to **3** in yields comparable to that of the two-step procedure. Electrophilic aromatic bromination with molecular bromine gives monomer **4**.[14] The 5,6-dialkoxy-4,7-dibromo-2,1,3-benzothiadiazole monomer **6**, the sulfur analogue of **4**, is obtained in three steps from the same starting material, 1,2-dialkoxy-4,5-dinitrobenzene **1** (Scheme 1). Reduction of the nitro groups with tin(II) dichloride gives the substituted *o*-phenylenediamine as its air-stable hydrochloride salt.[15] Treatment with *N*-thionylaniline affords **5**, which is brominated as for **4** to provide monomer **6** in excellent yield. The synthetic routes are likely applicable to a variety of alkyl and alkoxy side chains in the 5- and/or 6-positions.

A series of conjugated polymers were prepared by palladium-catalyzed cross-coupling polycondensation of dibromo monomers **4**, **6**, **10**[9,10] and monomers **7**, **8**, **9** (Scheme 2) to investigate the influence of these new heterocycles on the polymer properties (Table 1). Monomers **7** and **9** are typical comonomers commonly employed in the synthesis of poly(arylene ethynylene)s and polyfluorenes. Monomer **8** has been popularized for its aptitude to generate poly(arylene ethynylene)s that do not aggregate in the solid state.[16] The high yields and high molecular weights obtained using typical reaction conditions (5% $Pd(PPh_3)_4$ as catalyst, 65−90 °C) are indicative of the high reactivity of monomers **4**, **6**, and **10**, and of their suitability for incorporation into conjugated polymers.[17]

Polymers **P1** and **P2** are isolated with high mass recovery as red solids (Scheme **2**). Both polymers are soluble in chloroform at room temperature. In contrast, polymers prepared with the corresponding unsubstituted 2,1,3-benzooxadiazole (**10**) are strongly aggregated and do not redissolve even in boiling chlorobenzene, which illustrate the beneficial effect of flexible side chains at the 5,6-positions of the heterocycle on the solubility of the resulting polymers. Polymer **P1** is also fully soluble in hot tetrahydrofuran but is only partially soluble in the same solvent at room temperature, a factor that precludes the accurate measurement of its molecular weight by gel permeation chromatography. Polymer **P2**, isolated in high yield with an average degree

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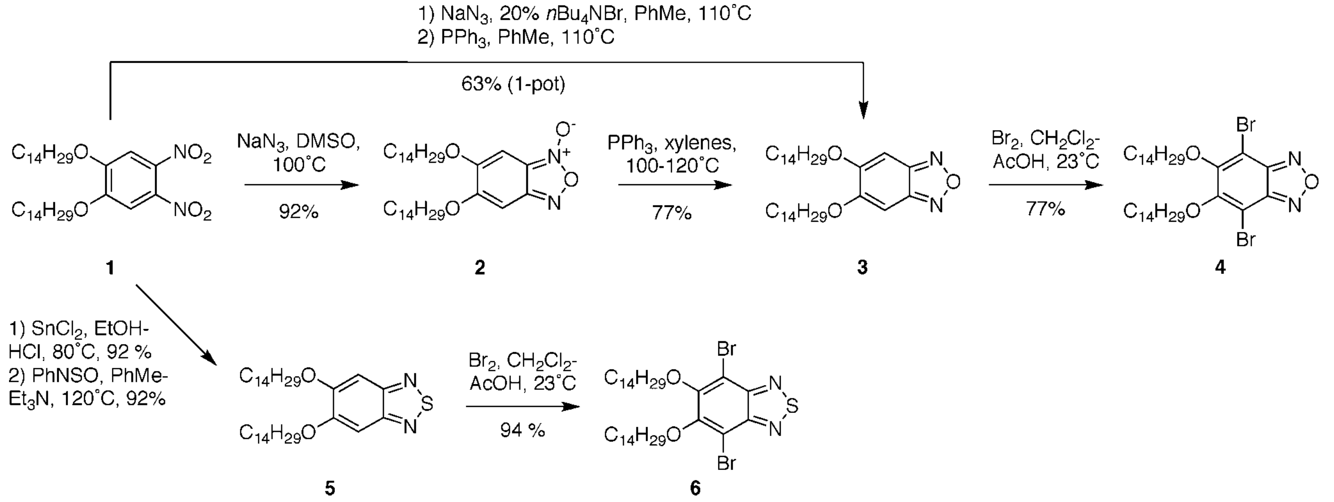
Scheme 1. Synthesis of 2,1,3-Benzooxadiazole Monomer 4 and 2,1,3-Benzothiadiazole Monomer 6



Scheme 2. Synthesis of Polymers P1−P7

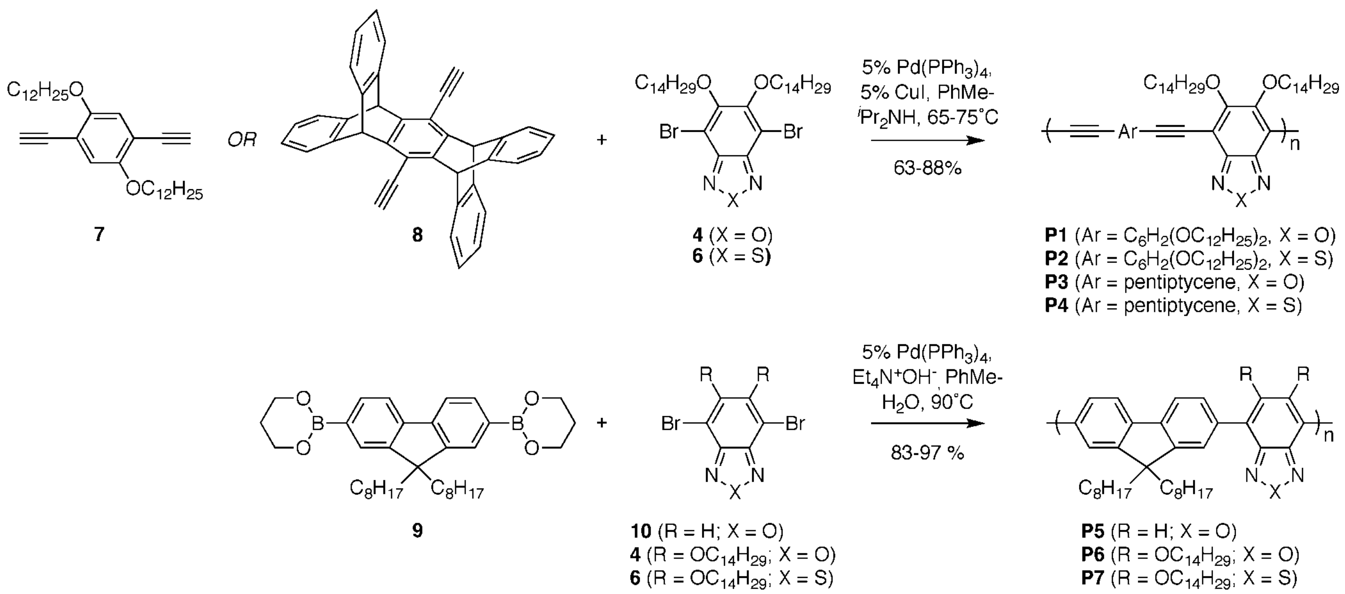


Table 1. Characterization and Spectroscopic Data for Polymers P1−P7 and Reference Polymers

		λ_{max} (nm)		λ_{em} (nm)		Φ_f	
polymer	M_n/M_w[a] (10^3 g mol^{-1})	solution ($CHCl_3$) (ε/L mol^{-1} cm^{-1})[c]	thin film	solution ($CHCl_3$)	thin film	solution ($CHCl_3$)	thin film[g]
P1	>5.4/8.3[b]	504 (34 000) [557 (23 000)][d]	554	554	586	0.31[e]	0.056
P2	21.0/84.3	499 (33 000)	543	550	579	0.35[e]	0.031
P3	29.7/66.3	494 (49 000)	500	516	523	0.58[e]	0.18
P4	24.6/59.8	498 (50 500)	502	518	526	0.64[e]	0.30
P5	30.0/77.9	475 (38 000)	489	536	546	0.50[e]	0.37
P6	46.7/102.0	421 (28 000)	429	517	498	0.51[f]	0.41
P7	55.6/135.9	416 (20 000)	424	513	498	0.48[f]	0.33
PPE-1[23]	98/144	452 (27 500)	–	482	–	0.40	–
PPE-2[23]	144/374	441 (–)	448	457	460	0.50	0.33
PF-1[23]	36/100	389 (–)	394	414	424	0.81	0.55

[a] Determined by GPC against PS standards. [b] Mostly insoluble in THF at room temperature; values given represent those of soluble oligomers. [c] Molar absorptivity based on the molecular weight of a repeating unit. [d] Aggregation band observed at higher concentrations in $CHCl_3$. See text for discussion. [e] Against coumarin 6 in EtOH ($\Phi_f = 0.78$, $\lambda_{ex} = 460$ nm).[20] [f] Against quinine sulfate in 1 N H_2SO_4 ($\Phi_f = 0.546$, $\lambda_{ex} = 366$ nm).[21] [g] Against perylene in PMMA ($\Phi_f = 0.87$, $\lambda_{ex} = 412$ nm).[22]

of polymerization of 20, is fully soluble in these solvents at room temperature. Polymers **P3** and **P4** which incorporate 6,13-diethynylpentiptycene (**8**) as a comonomer to prevent strong aggregation of the polymer chains were prepared according to the same procedures. The absence of solubilizing side chains (e.g., **8** + **10**) results in the precipitation of insoluble oligomers from the reaction mixture. However, polymers **P3** and **P4** are obtained as fully soluble yellow-orange solids with high molecular weights (>20 kg mol^{-1}). Polyfluorenes **P5**−**P7** that incorporate monomers **4**, **6**, and **10** were copolymerized with monomer **9** under previously described biphasic conditions for Suzuki−Miyaura cross-coupling polymerizations of fluorene derivatives.[18] Polymers **P5**−**P7** are isolated as highly soluble bright yellow (**P6** and

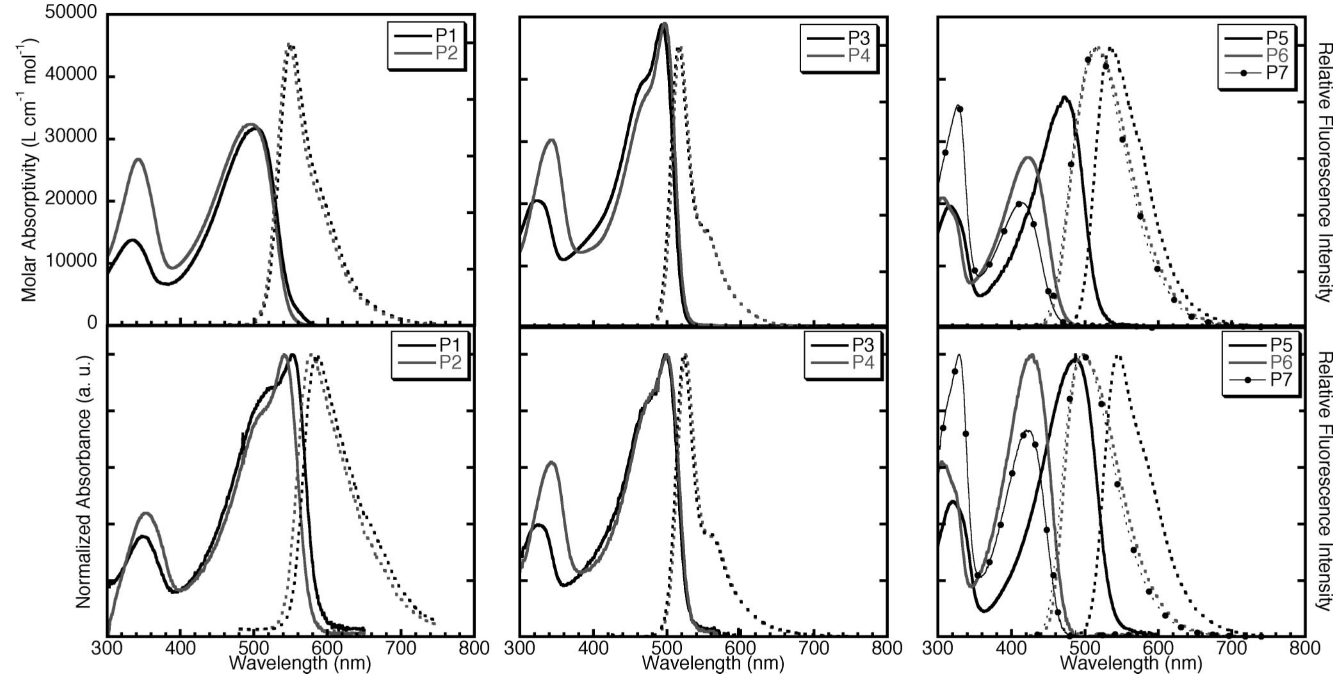
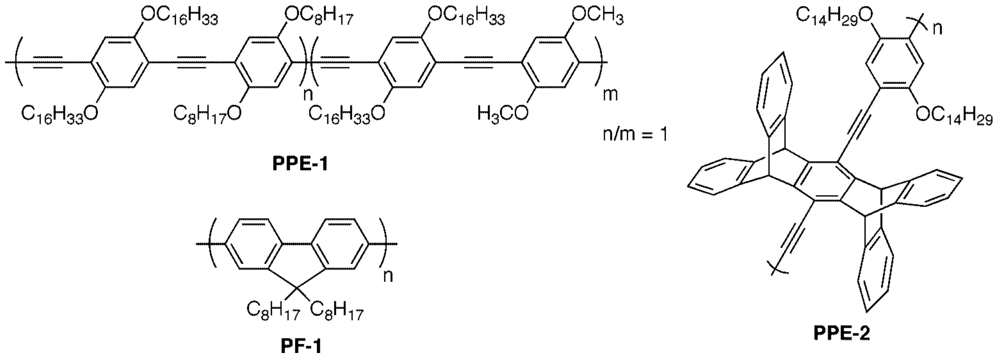


Figure 1. UV–vis (solid lines) and fluorescence (dashed lines) spectra of polymers **P1**–**P7** in chloroform solution (top) and in thin films (bottom).

Scheme 3. Reference Polymers[23]



P7) or orange (**P5**) high molecular weight materials (DP ~ 50–60).[19]

The absorption and fluorescence emission spectra for polymers **P1**–**P7** in chloroform solution are shown in Figure 1, and the summarized spectroscopic data are presented in Table 1. For the purpose of comparison, three conjugated polymers from the literature are also presented (Scheme 3, Table 1). The influence of the donor–acceptor character of the transitions on the optical properties of polymer **P1**–**P7** is significant. The polymers are considerably red-shifted in both absorption and emission maxima with respect to corresponding polymers that do not incorporate electron-deficient heterocycles,[23] and the extent of the bathochromic shift (50–90 nm) is proportional to the strength of the donor and acceptor groups. This analysis suggests that the electron-accepting strength of 2,1,3-benzothiadiazole is between that of monomers **4** and **10**, as expected on the basis of the higher electronegativity of oxygen relative to sulfur and the presence of the electron-donating alkoxy groups in **4**. Polymer **P1** does not aggregate in dilute chloroform solutions (3×10^{-6} mol L^{-1}); however, an aggregation band centered at 557 nm appears and grows as concentration is raised (>2×10^{-5} mol L^{-1}). Finally, polymers **P1** and **P2** in their unaggregated state are efficient fluorophores, with a fluorescence quantum yield of 0.31–0.35. These values are only slightly lower than that of corresponding PPEs that do not incorporate these heterocycles ($\Phi_f \sim 0.35$–0.40),[23] and this lower efficiency may be attributed to the effects of the energy gap law.[24] Similar trends are observed with polymers **P3** and **P4** which exhibit absorption and emission maxima that are red-shifted by 60–70 nm with respect to corresponding PPEs that do not incorporate these heterocycles.[23] These polymers do not exhibit evidence of aggregation either in solution or in the solid state, and high fluorescence quantum efficiencies are preserved in the solid state.

Polyfluorenes **P5**–**P7** are obtained as bright yellow (**P6, P7**) and orange (**P5**) solids that are fully soluble in organic solvents, including **P5** which incorporates monomer **10** which gave rise to insoluble polymers when polymerized with **7** or **8**. These heterocyclic polyfluorenes do not show evidence of aggregation either in solution or in the solid state. Aggregation is presumably limited by the presence of flexible side chains that are perpendicular to the plane of the fluorene monomer **9**, sterically preventing close stacking between the aromatic surfaces. As observed for the poly(arylene ethynylene)s, absorption and emission maxima are red-shifted when compared to polymers that do not incorporate these heterocycles, such as poly(9,9-dioctyl-9*H*-fluorene-2,7-diyl), **PF-1**, and the stronger donor–acceptor nature of **P5** causes a significantly greater red shift than is observed for either **P6** or **P7**. Interestingly, while most conjugated polymers exhibit bathochromic shifts from solution to the solid state, the emission spectra of polymers **P6** and **P7** exhibit hypsochromic shifts in thin films, which is indicative of a solid-state organization that disrupts the extent of conjugation. Nonetheless, polymers **P5**−**P7** are efficient fluorophores both in solution and in the solid state, with high fluorescence quantum yields (0.33−0.51).

Only small differences are found between spectroscopic properties polymers that incorporate monomer **4** (e.g., **P1**, **P3**, **P6**) and that of polymers that incorporate monomer **6** (e.g., **P2**, **P4**, **P7**). We consider this to be indicative of similar electronic properties of the two monomers.

Conclusions

New 2,1,3-benzooxadiazole and 2,1,3-benzothiadiazole electron-deficient monomers bearing solubilizing side chains have been synthesized in high yields over three steps from readily available starting materials. These monomers are efficiently incorporated with a variety of comonomers in cross-coupling polymerizations to afford high molecular weight luminescent conjugated polymers that exhibit red-shifted absorption and emission maxima, greater solubility, and reduced aggregation. The electronic properties of the new monomers and polymers are intermediate between those of common arylenes and those of unsubstituted 2,1,3-benzooxadiaxzoles and 2,1,3-benzothiadiazoles, offering potential for the fine-tuning of electronic properties without having to rely on adjustments in the feed ratios of comonomers to control the degree of energy migration to a lower band-gap emission site. The electron-deficient properties of these materials suggest potential applications as green-emitting polymers that facilitate electron injection in light-emitting devices.

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Supporting Information Available: Complete experimental procedures and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Pilgram, K.; Zupan, M.; Skiles, R. *J. Heterocycl. Chem.* **1970**, *7*, 629–633.

(2) (a) Huang, J.; Li, C.; Xia, Y.-J.; Zhu, X.-H.; Peng, J.; Cao, Y. *J. Org. Chem.* **2007**, *72*, 8580–8583. (b) Raimundo, J.-M.; Blanchard, P.; Brisset, H.; Akoudad, S.; Roncali, J. *Chem. Commun.* **2000**, 939–940. (c) Fang, Q.; Xu, B.; Jiang, B.; Fu, H.; Chen, X.; Cao, A. *Chem. Commun.* **2005**, 1468–1470.

(3) (a) Bernius, M. T.; Inbasekaran, M.; O'Brien, J.; Wu, W. *Adv. Mater.* **2000**, *12*, 1737–1750. (b) Bernius, M.; Inbasekaran, M.; Woo, E.; Wu, W.; Wujkowski, L. *J. Mater. Sci.: Mater. Electron.* **2000**, *11*, 111–116. (c) Liu, J.; Bu, L.; Dong, J.; Zhou, Q.; Gheng, Y.; Ma, D.; Wang, L.; Jing, X.; Wang, F. *J. Mater. Chem.* **2007**, *17*, 2832–2838. (d) Müller, C. D.; Falcou, A.; Reckefuss, N.; Rojahn, M.; Wiederhirn, V.; Rudali, P.; Frohne, H.; Nuyken, O.; Becker, H.; Meerholz, K. *Nature (London)* **2003**, *421*, 829–833. (e) Huang, J.; Niu, Y.; Yang, W.; Mo, Y.; Yuan, M.; Cao, Y. *Macromolecules* **2002**, *35*, 6080–6082. (f) Herguth, P.; Jiang, X.; Liu, M. S.; Jen, A. K.-Y. *Macromolecules* **2002**, *35*, 6094–6100. (g) Yang, R.; Garcia, A.; Korystov, D.; Mikhailovsky, A.; Bazan, G. C.; Nguyen, T.-Q. *J. Am. Chem. Soc.* **2006**, *128*, 16532–16539. (h) Millard, I. S. *Synth. Met.* **2000**, *111–112*, 119–123.

(4) Zhang, X.; Yamaguchi, R.; Moriyama, K.; Kadowaki, M.; Kobayashi, T.; Ishi-i, T.; Thiemann, T.; Mataka, S. *J. Mater. Chem.* **2006**, *16*, 736–740.

(5) Durmus, A.; Gunbas, G.; Camurlu, P.; Toppare, L. *Chem. Commun.* **2007**, 3246–3248.

(6) Bangcuyo, C. G.; Evans, U.; Myrick, M. L.; Bunz, U. H. F. *Macromolecules* **2001**, *34*, 7592–7594.

(7) (a) Liu, B.; Bazan, G. C. *J. Am. Chem. Soc.* **2004**, *126*, 1942–1943. (b) An, L.; Tang, Y.; Feng, F.; He, F.; Wang, S. *J. Mater. Chem.* **2007**, *17*, 4147–4152.

(8) Conjugated polymers that incorporate 2,1,3-benzoselenadiazole:(a) Chien, C.-H.; Shih, P.-I.; Shu, C.-F. *J. Polym. Chem. A* **2007**, *45*, 2938–2946. (b) Velusamy, M.; Thomas, R. K.; Lin, J. T.; Wen, Y. S. *Tetrahedron Lett.* **2005**, *46*, 7647–7651. (c) Li, X.; Zeng, W.; Xia, Y.; Yang, W.; Cao, Y. *J. Appl. Polym. Sci.* **2006**, *102*, 4321–4327. (d) Yasuda, T.; Imase, T.; Yamamoto, T. *Macromolecules* **2005**, *38*, 7378–7385. (e) Yang, J.; Jiang, C.; Zhang, Y.; Yang, R.; Yang, W.; Hou, Q.; Cao, Y. *Macromolecules* **2004**, *37*, 1211–1218. (f) Yang, R.; Tian, R.; Hou, Q.; Cao, Y. *Macromolecules* **2003**, *36*, 7453–7460. (g) Huang, F.; Hou, L.; Shen, H.; Yang, R.; Hou, Q.; Cao, Y. *J. Polym. Sci., Part A* **2006**, *44*, 2521–25321,2,3-Benzotriazole: (h) Tanimoto, A.; Yamamoto, T. *Adv. Synth. Catal.* **2004**, *346*, 1818–1823. (i) Tanimoto, A.; Yamamoto, T. *Macromolecules* **2006**, *39*, 3546–3552. (j) Sun, M.; Niu, Q.; Yang, R.; Du, B.; Liu, R.; Yang, W.; Peng, J.; Cao, Y. *Eur. Polym. J.* **2007**, *43*, 1916–1922. Naphthothiadiazole: (k) Qiu, Y.; Wei, P.; Zhang, D.; Qiau, J.; Duan, L.; Li, Y.; Cao, Y.; Wand, L. *Adv. Mater.* **2006**, *18*, 1607–1611. Naphthoselenadiazole: see ref 8e. Benzobis(thiadiazole): (l) Bundgaard, E.; Krebs, F. C. *Macromolecules* **2006**, *39*, 2823–2831. (m) Kitamura, C.; Tanaka, S.; Yamashita, Y. *Chem. Mater.* **1996**, *8*, 570–578.

(9) Blouin, N.; Michaud, A.; Gendron, D.; Wakim, S.; Blair, E.; Neagu-Plesu, R.; Belletête, M.; Durocher, G.; Tao, Y.; Leclerc, M. *J. Am. Chem. Soc.* **2008**, *130*, 732–742.

(10) (a) Qiu, Y.; Li, J.; Li, Y.; Gao, Y. CN 1840525, **2006**. (b) Becker, H.; Treacher, K.; Spreitzer, H.; Falcou, A.; Stoessel, P.; Buesing, A.; Parham, A. DE patent 10145553, **2003**. and affiliated international patents.

(11) Ghosh, P. B.; Whitehouse, M. W. *Biochem. J.* **1968**, *108*, 155–156.

(12) Takakis, I. M.; Hadjimihalakis, P. M.; Tsantali, G. G. *Tetrahedron* **1991**, *47*, 7157–7170, and references therein.

(13) Boyer, J. H.; Ellsey, S. E., Jr *J. Org. Chem.* **1961**, *26*, 4684–4685.

(14) Substitution at the 5,6-positions markedly affects the reactivity of the benzofurazans, as **3** reacts as a typical arene with electrophilic reagents (S_EAr) while unsubstituted benzofurazan reacts with bromine as a conjugated diene.

(15) Far, A. R.; Shivanyuk, A.; Rebek, J., Jr *J. Am. Chem. Soc.* **2002**, *124*, 2854–2855.

(16) (a) Yang, J.-S.; Swager, T. M. *J. Am. Chem. Soc.* **1998**, *120*, 5321–5322. (b) Yang, J.-S.; Swager, T. M. *J. Am. Chem. Soc.* **1998**, *120*, 11864–11873.

(17) Unactivated bromides are often insufficiently reactive in Sonogashira−Hagihara polymerizations, resulting in reduced yields and low molecular weights. Side reactions such as homocouplings can then become predominant as the reactivity of monomers decrease. See ref 6 and: (a) Swager, T. M.; Gil, C. J.; Wrighton, M. S. *J. Phys. Chem.* **1995**, *99*, 4886–4893. (b) Giesa, R.; Schulz, R. *Makromol. Chem.* **1990**, *191*, 857–867.

(18) Cho, S. Y.; Grimsdale, A. C.; Jones, D. J.; Watkins, S. E.; Holmes, A. B. *J. Am. Chem. Soc.* **2007**, *129*, 11910–11911.

(19) Polymer **P5** has been reported in research accounts from Dow Chemical (see refs 3a and 3b), but details of its preparation, characterization, and properties were not given.

(20) Reynolds, G. A.; Drexhage, K. H. *Opt. Commun.* **1975**, *13*, 222–225.

(21) (a) Olmsted, J., III *J. Phys. Chem.* **1979**, *83*, 2581–2584. (b) Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991–1024. (c) Melhuish, W. H. *J. Phys. Chem.* **1961**, *65*, 229–235. (d) Dawson, W. R.; Windsor, M. W. *J. Phys. Chem.* **1968**, *72*, 3251–3260.

(22) Melhuish, W. H. *J. Opt. Soc. Am.* **1964**, *52*, 183–186.

(23) See Supporting Information for comparisons with reference polymers that do not incorporate heterocycles. Poly(1,4-dialkoxybenzene-2,5-ylethynylene) (**PPE-1**): refs 17a, b. Pentiptycene-containing **PPE-2**: refs 16a, b. Poly(9,9-dioctyl-9*H*-fluorene-2,7-diyl) (**PF-1**):Lim, E.; Jung, B.-J.; Shim, H.-K. *Macromolecules* **2003**, *36*, 4288–4293.

(24) Ishow, E.; Bouffard, J.; Kim, Y.; Swager, T. M. *Macromolecules* **2006**, *39*, 7854–7858.

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